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SYNTHESIS OF SYEP PLASTICIZER

Flurochem, Inc.  
6233 N. Irwindale Avenue  
Azusa, California 91702

October 1975

Final Report for Period August 1974 - August 1975

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Prepared for

AIR FORCE ROCKET PROPULSION LABORATORY  
DIRECTOR OF SCIENCE AND TECHNOLOGY  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
EDWARDS AIR FORCE BASE, CALIFORNIA 93523

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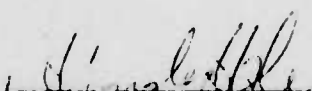
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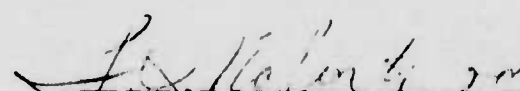
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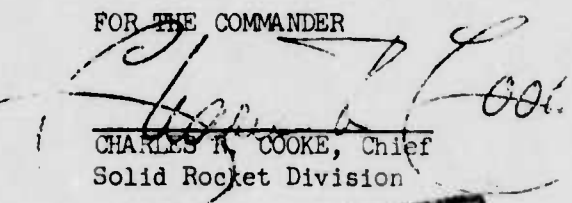
This report was submitted by Fluorochem, Inc., 6233 Irwindale Avenue, Azusa, California 91702, under Contract FO4611-75-C-0003, Job Order No. with the Air Force Rocket Propulsion Laboratory, Edwards, CA 93523.

This technical report has been reviewed and is approved for publication.

  
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>SYEP, a new plasticizer was synthesized by difluoramination of 1,3-bis-fluorodinitroethoxy)acetone. Phase I of this program involved demonstration of the feasibility of this synthesis and determination of physical properties of SYEP. Phase II dealt with study of reaction variables with emphasis of improving the yield of 1,3-bis(fluorodinitroethoxy)isopropanol, the key-intermediate, from fluorodinitroethanol and epichlorohydrin, and its oxidation to 1,3-bis(fluorodinitroethoxy)acetone. One hundred grams of SYEP was synthe- |                       |  |

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(20) Abstract

→ sized during Phase II. Phase III involved a scale-up operation which resulted in production of 5 lb of SYEP. ←

(UNCLASSIFIED ABSTRACT)

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## PREFACE

This technical report summarizes the work accomplished under Air Force Contract FO4611-75-C-0003 between August 1974 through August 1975 by Fluorochem, Inc., 6233 N. Irwindale Avenue, Azusa, California.

This work was sponsored by the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base. Mr. N. J. Vanderhyde (MKPA) was the Contract Monitor. The effort reported herein was funded in part by In-House Laboratory Independent Research Funds.

Contributors to this program included: Dr. V. Grakauskas, Program Manager and responsible scientist; Dr. K. Baum, Dr. N. N. Ogimachi, and Mr. T. R. Malefy.



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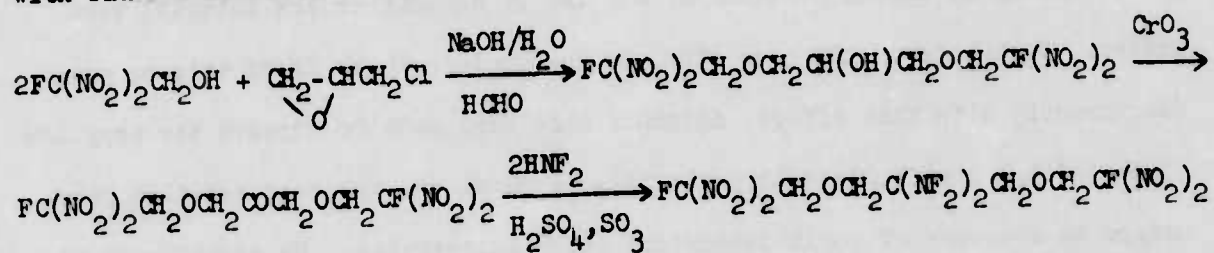
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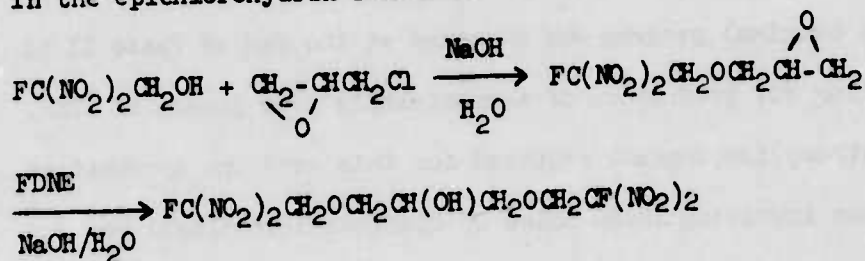
## SECTION I

### SUMMARY

This report describes the synthesis of 1,3-bis(fluorodinitroethoxy)-2,2-bis(difluoramino)propane, SYEP (SYmmetrical fluorodinitroEthoxy Propane), a new high energy plasticizer, by the following three-step reaction scheme starting with fluorodinitroethanol (FDNE):



The isopropanol is synthesized in 12-15% yields by reacting an alkaline aqueous formaldehyde solution of fluorodinitroethanol with either epichlorohydrin or with fluorodinitroethyl glycidyl ether. The glycidyl ether is the intermediate in the epichlorohydrin reaction.



This program consisted of three phases: Phase I, feasibility study, Phase II, study of reaction variables and synthesis of 100 g of SYEP, and Phase III, production of five pounds of SYEP.

Phase I involved the feasibility study of difluoramination of 1,3-bis-(fluorodinitroethoxy)acetone first synthesized at Fluorochem a few years ago. During the first two months of this program it was shown that this ketone reacts smoothly with two moles of difluoramine in 30% fuming sulfuric acid to give SYEP which was fully characterized.

Preliminary physical and chemical properties indicated that SYEP might indeed become an useful plasticizer and larger amounts of the material were needed. Synthesis of 100 g of SYEP was the goal of Phase II of this program. Concurrently with this effort, attempts also were made to improve the very low yields of 1,3-bis(fluorodinitroethoxy)isopropanol by exploring reaction parameters in a number of small laboratory scale experiments. No significant improvement materialized in this limited study but the experiments provided enough 1,3-bis(fluorodinitroethoxy)isopropanol needed for the synthesis of 100 g of SYEP. With the anticipation of a further scale-up, a number of process improvements were made during this study.

The scope of the original program was expanded at the end of Phase II to include Phase III calling for production of approximately five pounds of SYEP. 1,3-Bis(fluorodinitroethoxy)isopropanol required for this task was synthesized in five large-scale runs involving 12-20 moles of fluorodinitroethanol per run. Liquid extraction of the crude material provided a prepurified alcohol suitable for oxidation to 1,3-bis(fluorodinitroethoxy)acetone. Crude 1,3-bis(fluorodinitroethoxy)acetone was purified by silica gel chromatography, followed by

crystallization from chloroform to give high purity material needed for the difluoramination reaction.

Large scale difluoramination of 1,3-bis(fluorodinitroethoxy)acetone, carried out remotely in eight 0.5-0.75 lb runs, proceeded quantitatively and gave SYEP of excellent purity (98%+).

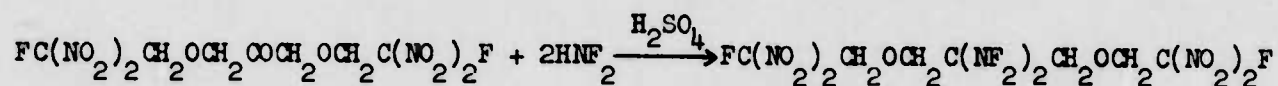
## SECTION II

### INTRODUCTION

Compounds containing both fluorodinitro and geminal bis(difluoramino) functions are finding applications in formulations of advanced energetic propellants. The basic reactions for producing these high-energy functional groups are direct fluorination of dinitrocompounds (Ref. 1) and reaction of ketones with difluoramine (Ref. 2).

Because the ether function usually leads to good low temperature properties and chemical stability of energetic molecules, it was desirable to synthesize an ether containing the maximum number of these energetic groups. The target compound of this study was 1,3-bis(fluorodinitroethoxy)-2,2-bis(difluoramino)propane.

Phase I of this program initiated August 1974 was designed to demonstrate the feasibility of synthesis of this propane derivative by difluoramination of 1,3-bis(fluorodinitroethoxy)acetone synthesized at Fluorochem in 1973 (Ref. 3):



This synthesis was accomplished during the first two months of this program.

The physical and chemical properties of the compound designated by the acronym SYEP (Symmetrical fluorodinitroEthoxy Propane) seemed to meet all the expectations, and the next phase of the program involved synthesis of 100 g of SYEP for further evaluation of its properties. Phase II was completed in January 1975 at

which time the contract was amended to include the synthesis of 5 lb of SYEP.  
This third phase was successfully completed in August 1975.

The details of this work presented in the following section are organized chronologically following the three phases of the program.

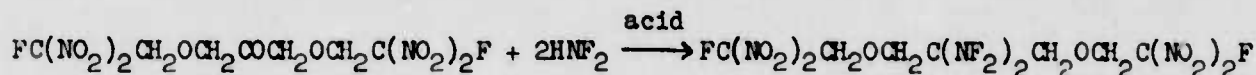


### SECTION III

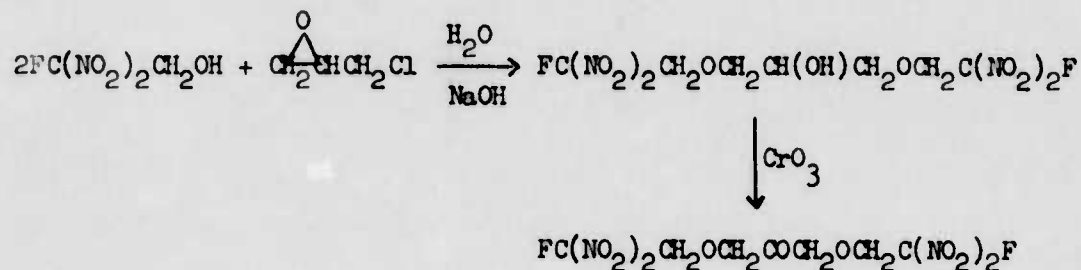
#### TECHNICAL DISCUSSION

##### FEASIBILITY STUDY

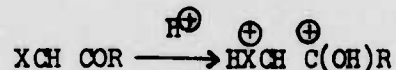
The proposed synthesis of SYEP required difluoramination of 1,3-bis(fluorodinitroethoxy)acetone with difluoramine in a strong acid medium:



1,3-Bis(fluorodinitroethoxy)acetone was first synthesized at Fluorochem in 1973 (Ref. 3) in a two-step reaction by reacting epichlorohydrin with two moles of fluorodinitroethanol in aqueous alkali to give 1,3-bis(fluorodinitroethoxy)isopropanol, followed by oxidation of the alcohol:



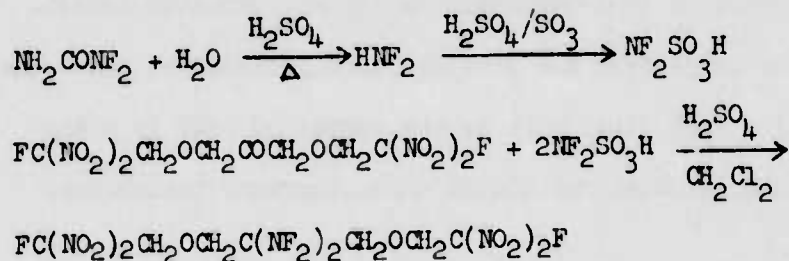
The reaction of ketones with difluoramine to give the corresponding geminal bis(difluoramino) derivatives (Ref. 1) is sensitive to the electronic properties of substituents (Ref. 4). Substituents that are protonated readily retard reaction because of energetically unfavorable dications:



Relatively subtle changes can mean the difference between success and failure

of the reaction. Thus, acetyl acetate does not give geminal difluoramino derivative, whereas acetyl trifluoroacetate does. The electron-withdrawing effect of the fluorines is sufficient to prevent protonation of the ester group, but not so great as to deactivate the carbonyl group. 1,3-Bis(fluorodinitroethoxy)acetone offered a reasonable possibility of undergoing difluoramination because of the electron-withdrawing nitro and fluoro substituents.

Although some problems were anticipated with difluoramination of 1,3-bis(fluorodinitroethoxy)acetone, the reaction proceeded satisfactory the very first time we attempted it. In this reaction difluoramine generated from aqueous difluorourea (Ref. 5) was passed into 30% fuming sulfuric acid to give difluoraminosulfamic acid (Ref. 6). A methylene chloride solution of 1,3-bis(fluorodinitroethoxy)acetone was then added to the difluoraminosulfamic-sulfuric acid mixture and the reaction was allowed to proceed for a few hours at ambient temperature. The organic phase containing SYEP was separated, washed and dried to give a practically quantitative yield of the compound:



The compound, a colorless liquid somewhat less viscous than FEFO,  $d = 1.65$ , was characterized by elemental analysis and by proton and fluorine nmr spectra (see

Experimental).

The following additional physical properties of SYEP were obtained at the Lawrence Livermore Laboratory\*. Differential thermal analysis: exotherm starts at 157°, maximum at 245°. Impact sensitivity: drop hammer (2.5 kg), 1/8" gap (without sandpaper), 30 cm. Freezing point -2.5°. Boiling point ca 120° at 10<sup>-5</sup> Torr (slight decomposition). Thermal stability: two 0.25 g samples heated at 120° for 22 hrs liberated 1.60 and 1.91 cc of gas, respectively.

At the beginning of this work some problems were encountered with the purity of SYEP which soon were traced to the impurities present in the starting material, 1,3-bis(fluorodinitroethoxy)acetone. Subsequently, when the high purity ketone became available difluoramination reactions proceeded quantitatively and gave SYEP of excellent purity (98%+).

In all our work the SYEP was analyzed by nmr. Both, the proton (a doublet and a singlet) and fluorine (a triplet and a singlet) spectra of SYEP are very simple and using concentrated solutions of the material in order to suppress the background noise, impurities present in 1-2% concentration are probably detectable. Nmr analyses are simple to perform and provide quick information about the purity of SYEP. More extensive analytical work on the purity of SYEP is being conducted at RPL with particular emphasis on liquid chromatography techniques.

#### STUDY OF REACTION VARIABLES

When the feasibility of synthesizing SYEP was demonstrated, the next phase

\* We thank Mr. M. Finger and Dr. R. Elson for making this data available to us for this report.

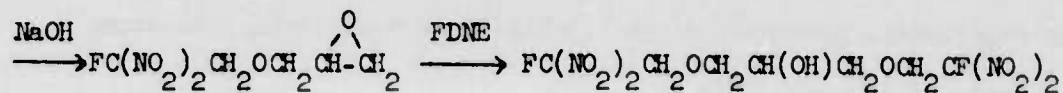
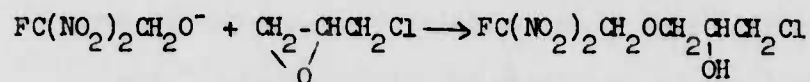
of work called for the preparation of 100 g of the material discussed in this section. Prior to this effort a large number of laboratory experiments were carried out in an attempt to increase the yields of intermediates. These small scale experiments provided enough 1,3-bis(fluorodinitroethoxy)acetone for the synthesis of 100 g of SYEP.

Two major problems were encountered in the synthesis of larger amounts of SYEP: (1) poor yields of 1,3-bis(fluorodinitroethoxy)isopropanol, the precursor of 1,3-bis(fluorodinitroethoxy)acetone, from fluorodinitroethanol and epichlorohydrin, and (2) difficulties with purification of 1,3-bis(fluorodinitroethoxy)acetone. Approaches explored to remedy these two problems and the results are discussed below.

#### 1,3-Bis(fluorodinitroethoxy)isopropanol

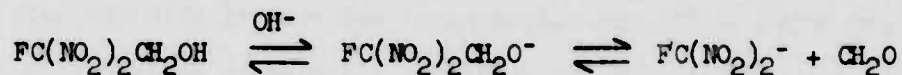
1,3-Bis(fluorodinitroethoxy)isopropanol is synthesized from fluorodinitroethanol and epichlorohydrin in either one or two steps (Ref. 3). In the one step route two moles of fluorodinitroethanol are reacted with one mole of epichlorohydrin in aqueous alkaline formaldehyde solution at ambient temperature. This reaction is very slow and several days are needed for its completion. It proceeds by a nucleophilic attack by fluorodinitroethoxy ion on the epoxide to give the corresponding halohydrin intermediate, 1-(fluorodinitroethoxy)-3-chloroisopropanol which is cyclized to fluorodinitroethyl glycidyl ether by the base. The glycidyl ether then reacts with fluorodinitroethanol to give 1,3-bis-

(fluorodinitroethoxy)isopropanol:



In the two step reaction scheme, fluorodinitroethyl glycidyl ether prepared separately by several available routes, including the fluorodinitroethyl-epichlorohydrin reaction, is reacted with a molar amount of fluorodinitroethanol in the presence of sodium hydroxide, again in aqueous formaldehyde. Several days are needed to complete this reaction.

In aqueous alkaline solution fluorodinitroethanol is known to be in equilibrium with formaldehyde and fluorodinitromethane anion (Ref. 7). Excess of formaldehyde reduces the concentration of the unstable fluorodinitromethane anion by mass action:



Formaldehyde slows down considerably the decomposition of fluorodinitroethanol and allows longer reaction times and higher reaction temperatures. Nevertheless, over a period of several days, the time period needed for fluorodinitroethanol reactions with epoxides to go to completion at ambient temperatures, a large amount of the alcohol decomposes. Decomposition of fluorodinitroethanol

accelerates rapidly with increasing reaction temperatures, so that a practical reaction temperature is the ambient.

Large amounts of formaldehyde used to stabilize fluorodinitroethanol, however, result in the contamination by polyoxymethylene polymers of various molecular weights. These contaminants usually amount to 30-50% of the weight of crude product.

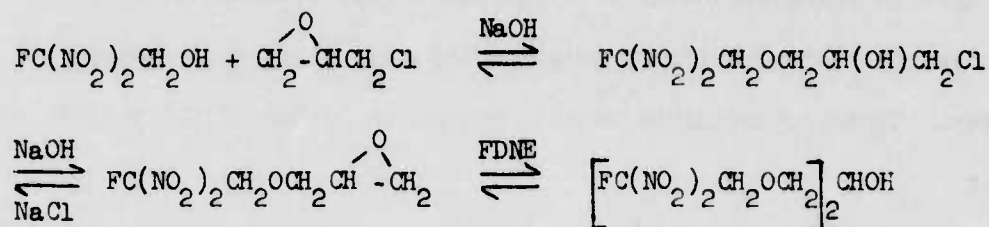
The yields of fluorodinitroethanol-epihalohydrin reactions are low. The originally reported 31% yield of fluorodinitroethyl glycidyl ether in epichlorohydrin reaction with fluorodinitroethanol (Ref. 8) could not be improved significantly in a subsequent extensive scale-up work (Ref. 9). This present work indicates that the originally reported 41% yield of 1,3-bis(fluorodinitroethoxy)-isopropanol in the reaction of fluorodinitroethyl glycidyl ether with fluorodinitroethanol also could not be significantly improved. Therefore, the yields of 1,3-bis(fluorodinitroethoxy)isopropanol in this two step reaction would be expected to be in the range of 12-13%.

A number of small scale experiments were carried out attempting to improving the yield in either of these two steps.

The reaction between fluorodinitroethanol and epichlorohydrin in aqueous alkaline formaldehyde, whether at a 1:1 or at a 2:1 molar ratio yields a mixture of fluorodinitroethyl glycidyl ether, 1-(fluorodinitroethoxy)-3-chloroisopropanol, and 1,3-bis(fluorodinitroethoxy)isopropanol in varying ratios. All these three compounds are present in the crude reaction product obtained under a



number of widely varying reaction conditions. Each of these three compounds is gradually degraded by aqueous alkali. There is some reason to believe that reactions leading to these three products all are reversible:



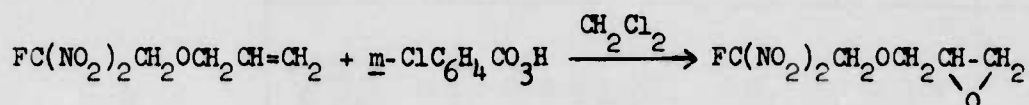
This being the case, fluorodinitroethanol-epichlorohydrin reactions slowly arrives at an equilibrium, but with a significant loss of fluorodinitroethanol. Large amounts of impurities introduced by formaldehyde make difficult to study this reaction quantitatively.

Epichlorohydrin homologues containing better leaving groups than chlorine, such as epibromohydrin, glycidyl methanesulfonate and glycidyl trifluoromethane sulfonate react with fluorodinitroethanol at about the same rate as epichlorohydrin. Thus, for example, glycidyl methanesulfonate reacted very slowly with fluorodinitroethanol in aqueous alkaline solution and after 3 days at ambient temperature ca 70% of the unreacted starting material was recovered. The methanesulfonate failed to react with the alcohol in chloroform solution using anhydrous potassium carbonate as the base. Glycidyl trifluoromethanesulfonate, prepared by reacting glycidol with trifluoromethanesulfonic acid anhydride, behaved similarly.

Other routes to fluorodinitroethyl glycidyl ether were explored in this



work. It was found that allyl fluorodinitroethyl ether can be readily oxidized to fluorodinitroethyl glycidyl ether in 90% yields with m-chloroperbenzoic acid in a methylene chloride or chloroform solution:



The originally reported (Ref. 8) 34% yield of allyl fluorodinitroethyl ether in fluorodinitroethanol-allyl bromide reaction was improved to 60-65%. Therefore, the overall yield of fluorodinitroethyl glycidyl ether via this two step route amounts to 55-60%, almost double of that realized in the fluorodinitroethanol reaction with epichlorohydrin. However, this process required handling of rather impact sensitive allyl fluorodinitroethyl ether and uses expensive m-chloroperbenzoic acid.

Considering all the problems associated with the synthesis of fluorodinitroethyl glycidyl ether, it became apparent that at least for this relatively small scale-up work, the one step synthesis of 1,3-bis(fluorodinitroethoxy)isopropanol is still the best route, and the remaining time was devoted to optimizing reaction conditions for maximum yield of the alcohol in this reaction. The results of this work are summarized in Table 1.

The best reaction conditions for the synthesis of 1,3-bis(fluorodinitroethoxy)isopropanol involved reacting two moles of fluorodinitroethanol with one mole of epichlorohydrin in ca 500 ml of 37% aqueous formaldehyde and two moles of sodium hydroxide (as 50% aqueous solution) at ambient temperature for a

Table 1. 1,3-Bis(fluorodinitroethoxy)acetone (Laboratory Scale)

| Run No.          | FDME |      | Epichlor. |      | NaOH             |      | 37% HNO <sub>3</sub> | H <sub>2</sub> O | Phase a) Transf. Cat. | React temp °C | React time hrs | Meth. ml | Crude Isoprop.    | Crude Ketone | Pure Ketone | Yield % |
|------------------|------|------|-----------|------|------------------|------|----------------------|------------------|-----------------------|---------------|----------------|----------|-------------------|--------------|-------------|---------|
| 1                | 185  | 1.2  | 40        | 0.43 | 86 <sup>b)</sup> | 1.3  | 350                  | 50               | 1                     | 23-25         | 23             | -        | 105               | 93           | 50          | 16      |
| 2                | 925  | 0.6  | 23        | 0.25 | 24               | 0.6  | -                    | 230              | 3                     | 0             | 8              | -        | 50                | -            | -           | -       |
| 3                | 308  | 2.0  | 80        | 0.86 | 82               | 2.05 | 500                  | 80               | 0.6                   | 25            | 48             | -        | 165               | -            | -           | -       |
| 4                | 325  | 2.11 | 80        | 0.86 | 65               | 2.1  | 500                  | 85               | 0.6                   | 23-25         | 88             | -        | 165               | 85           | 45          | -       |
| 5                | 465  | 3.0  | 120       | 1.3  | 125              | 3.1  | 750                  | 135              | 5                     | 23-25         | 88             | -        | 275               | -            | -           | -       |
| 6                | 165  | 1.06 | 46        | 0.5  | 40               | 1.0  | 800                  | 40               | -                     | 25            | 92             | 75       | 80                | 160          | 80          | -       |
| 7                | 330  | 2.1  | 92        | 1.0  | 80               | 2.0  | 2500                 | 80               | -                     | 25            | 92             | -        | 140               | -            | -           | -       |
| 8                | 330  | 2.1  | 142       | 1.54 | 80               | 2.0  | 2000                 | 80               | -                     | 24            | 110            | 250      | 210               | -            | -           | -       |
| 9                | 1186 | 7.7  | 453       | 4.9  | 300              | 7.5  | 3500                 | 280              | -                     | 25            | 144            | 500      | 956               | 400          | -           | -       |
| 10               | 930  | 6.0  | 444       | 4.8  | 240              | 6    | 6000                 | 240              | -                     | 20            | 170            | 700      | 584               | -            | -           | -       |
| 11               | 465  | 3.0  | 185       | 2.0  | 120              | 3    | 3000                 | 120              | -                     | 25            | 168            | 250      | 250               | -            | -           | -       |
| 12               | 925  | 6    | 350       | 3.75 | 240              | 6    | 4500                 | 240              | -                     | 25            | 168            | 500      | 500               | 116          | -           | -       |
| 13               | 310  | 2.0  | 100       | 1.1  | 82               | 2.1  | 600                  | 80               | 1.2                   | 25            | 48             | -        | 225 <sup>c)</sup> | -            | -           | -       |
| 14               | 310  | 2.0  | 120       | 1.3  | 80               | 2.0  | 1500                 | 80               | -                     | 25            | 90             | 150      | 142               | 211          | 65          | -       |
| 15               | 310  | 2.0  | 120       | 1.3  | 80               | 2.0  | 1500                 | 80               | -                     | 25            | 88             | 150      | 145               | -            | -           | -       |
| 16 <sup>d)</sup> | 625  | 4.0  | 220       | 2.4  | 160              | 4.0  | 3000                 | 160              | -                     | 25            | 68             | 250      | 365               | 880          | 190         | 9       |
| 17               | 625  | 4.0  | 220       | 2.4  | 180              | 4.5  | 2500                 | 160              | -                     | 25            | 65             | 250      | 368               | -            | -           | -       |
| 18               | 625  | 4.0  | 220       | 2.4  | 180              | 4.5  | 2500                 | 160              | -                     | 25            | 65             | 250      | 385               | -            | -           | -       |

a) Methyl tricapyryl ammonium chloride

b) KOH

c) Material degassed at 130-140° (0.2 mm) before oxidation

d) Materials of batches 16, 17, and 18 were combined and used in the scale-up run.

period of two to three days with efficient stirring. A small amount of phase-transfer catalyst, methyl tricaprylyl ammonium chloride, was employed in most runs. For the first several hours this reaction is mildly exothermic and some cooling may be required. The other details of this reaction are presented in the Experimental Section.

The weight of crude material obtained in the above reactions usually amounts to 90% of the weight of fluorodinitroethanol employed in a run. However, 1,3-bis(fluorodinitroethoxy)isopropanol is a minor component in this mixture.

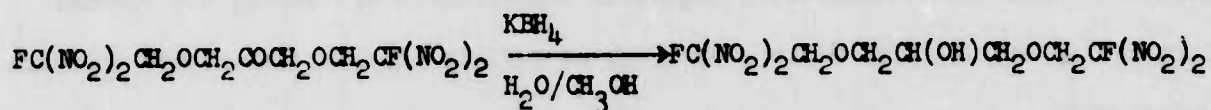
Crude 1,3-bis(fluorodinitroethoxy)isopropanol has been oxidized to 1,3-bis(fluorodinitroethoxy)acetone. However, a number of problems arose in these oxidations using highly impure material, and it became apparent that some type of prepurification of the alcohol was needed. A number of simple potential techniques such as crystallization, washing, attempting to prepare crystallizable derivatives, and others were explored, but the most practical were distillation and liquid-liquid extraction.

When crude 1,3-bis(fluorodinitro)isopropanol as obtained in the one-step reaction above is subjected to high temperature vacuum distillation both fluorodinitroethyl glycidyl ether, bp 70° (0.1 mm), and 1-(fluorodinitroethoxy)-3-chloroisopropanol, bp 110° (0.1 mm), can be removed. For an effective distillation of this viscous material, high bath temperatures are needed and thermal instability of aliphatic nitro compounds, as well as epoxides makes this approach undesirable.

A much more satisfactory purification technique was subsequently developed and adopted for larger scale operations. This technique involves extraction of crude 1,3-bis(fluorodinitroethoxy)isopropanol with carbon tetrachloride in a liquid-liquid extractor. The fluorodinitroethyl glycidyl ether and part of the 1-(fluorodinitroethoxy)-3-chloroisopropanol are extracted by carbon tetrachloride (bottom phase), whereas the isopropanol derivative and the bulk of polyoxymethylenes remain in the upper layer. This extraction is completed in 6-12 hrs, depending on the rate of circulation of carbon tetrachloride. Generally, the crude mixture loses 40% of its original weight in this extraction. The extract freed of the solvent can be recycled in the synthesis of 1,3-bis(fluorodinitroethoxy)isopropanol.

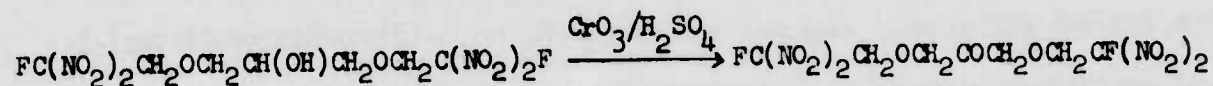
The carbon tetrachloride-extracted isopropanol derivative, now free of the glycidyl ether, but still containing large amounts of polyoxymethylenes and a sizable amount of 1-(fluorodinitroethoxy)-3-chloroisopropanol, is now suitable for oxidation to 1,3-bis(fluorodinitroethoxy)acetone.

In connection with the synthesis of 1,3-bis(fluorodinitroethoxy)isopropanol, a pure sample of the alcohol was needed. A column chromatographic purification of the crude material obtained in the reaction of fluorodinitroethanol with epichlorohydrin was not satisfactory. A very pure material was obtained in 85% yields by reduction of 1,3-bis(fluorodinitroethoxy)acetone with potassium borohydride:



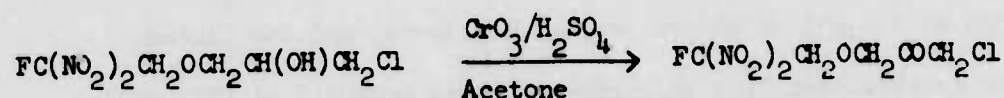
### 1,3-Bis(fluorodinitroethoxy)acetone

The Jones reagent (Ref. 10), chromium trioxide in sulfuric acid and acetone, was selected for the oxidation of 1,3-bis(fluorodinitroethoxy)isopropanol to 1,3-bis(fluorodinitroethoxy)acetone. The yield of this oxidation was found to be 95-100% when pure alcohol is used.



One drawback of this oxidation is the flammability hazard of the solvent. Other oxidizing agents such as aqueous dichromate or glacial acetic acid solution of chromium trioxide briefly investigated appeared less satisfactory. Since for the purpose of this relatively small scale work the flammability of acetone did not constitute a serious problem, the Jones reagent was used in all oxidation work.

1,3-Bis(fluorodinitroethoxy)isopropanol undergoes rapid oxidation with the Jones reagent at 5-25°. Polyoxymethylene present in the crude material do not seem to interfere with this oxidation. 1-(Fluorodinitroethoxy)-3-chloroisopropanol, on the other hand, is oxidized to 1-(fluorodinitroethoxy)-3-chloroacetone (Ref. 3):



The crude 1,3-bis(fluorodinitroethoxy)acetone thus is contaminated with



ca 30-50% polyoxymethylenes and by 10-30% of 1-(fluorodinitroethoxy)-3-chloroacetone. Only approximately 25% of the crude product is the desired ketone. A number of purification approaches were explored during the early stages of this work, but most of them were found unsatisfactory. The most acceptable procedure was column chromatography using silica gel and methylene chloride as the eluent. This method effectively removed polyoxymethylene impurities, but did not efficiently separate the two ketones. 1-(fluorodinitroethoxy)-3-chloroacetone undergoes difluoramination to give a relatively unstable product which impairs the thermal stability of SYEP and therefore the chloroketone must be rigorously excluded. The lower molecular weight ketone could be removed by high temperature vacuum distillation, but because of very high bath temperatures (140-150°), this approach was not practical. One batch of relatively pure 1,3-bis(fluorodinitroethoxy)acetone crystallized on prolonged standing. Consequently, with the availability of seed crystals the ketone was conveniently crystallized from chloroform to give a snow-white crystalline solid, mp 37°. 1-(Fluorodinitroethoxy)-3-chloroacetone is soluble in chloroform, and even at high concentrations remains in solution. Thus, the purification of 1,3-bis(fluorodinitroethoxy)acetone was accomplished as follows. The crude product, obtained in the oxidation of the isopropanol derivative, is passed through silica gel to remove polyoxymethylenes, and the eluted material is then crystallized from chloroform to give pure 1,3-bis(fluorodinitroethoxy)acetone.

The overall yields of crystallized 1,3-bis(fluorodinitroethoxy)acetone obtained in the above small scale reactions, based on fluorodinitroethanol, amounted to 11-14%. This yield does not include the recovered fluorodinitroethyl glycidyl ether in the extraction of the crude 1,3-bis(fluorodinitroethoxy)isopropanol which when recycled would increase the yield.

#### 1,3-Bis(fluorodinitroethoxy)-2,2-bis(difluoramino)propane (SYEP)

The synthesis of SYEP by difluoramination of 1,3-bis(fluorodinitroethoxy)acetone is relatively simple when the high purity ketone is available. The investigation of reaction parameters discussed above gave sufficient good quality 1,3-bis(fluorodinitroethoxy)acetone to synthesize the required 100 g of SYEP. The synthesis was accomplished in 10-20 g lots using a small laboratory unit described in details in The Experimental Section. The experience gained in this operation was helpful in designing a larger production scale difluoramination unit.

#### SCALE-UP WORK

The last phase of this program called for the production of approximately 5 pounds of SYEP. The material was successfully synthesized and the details of this scale-up work are summarized below.

#### 1,3-Bis(fluorodinitroethoxy)isopropanol

One 12 mole and two 20 mole runs were conducted by the procedure described



above. Another 12 mole run was carried out using fluorodinitroethyl glycidyl ether recovered from the three above runs. A small additional amount of the isopropanol was obtained by combining the material of three exploratory four mole runs. The details of these experiments are summarized in Table 2. No problems were encountered with this scaleup, and, generally, these larger scale runs gave yields similar to those of small laboratory experiments. The preparation of 1,3-bis(fluorodinitroethoxy)isopropanol probably could be readily scaled up further.

The crude 1,3-bis(fluorodinitroethoxy)isopropanol synthesized above was purified by extracting the crude mixture with carbon tetrachloride in a four liter liquid-liquid extractor fabricated of 3" OD glass tubing. Each isopropanol batch was treated separately and the progress of an extraction was followed by nmr and also by volume changes. Generally, the crude isopropanol lost 50% of its original weight in these extractions. The extraction data is given in Table 2.

The extracts of the first three runs were combined and concentrated to remove carbon tetrachloride. The concentrated material containing fluorodinitroethyl glycidyl ether as the major component was recycled in a reaction with fluorodinitroethanol (run 5 in Table 2) to synthesize another large batch of 1,3-bis(fluorodinitroethoxy)isopropanol.

Three small identical 4 mole batches of 1,3-bis(fluorodinitroethoxy)isopropanol were combined (batch 4) and the crude product was not extracted but

Table 2. 1,3-Bis(fluorodinitroethoxy)isopropanol (Pilot Runs)

| Run No. | FDNE, moles | Epichlor moles | 37% Formal., ml | NaOH, moles | React Temp, °C | React time, hrs | Yield g (crude p) | Yield g (aft.extr) | Remarks |
|---------|-------------|----------------|-----------------|-------------|----------------|-----------------|-------------------|--------------------|---------|
| 1       | 12          | 6.1            | 3600            | 12.3        | 25             | 45              | 1611              | 840                |         |
| 2       | 20          | 10.8           | 6000            | 20.5        | 23-5           | 46              | 2854              | 1584               |         |
| 3       | 20          | 10.8           | 6000            | 20.5        | 25             | 50              | 2402              | 1290               | *       |
| 4       | 12          | 12.8           | 6000            | 12.0        | 23             | 48              | 1100              | not extr.          | **      |
| 5       | 12          | -              | 6000            | 6.5         | 23             | 48              | 2870              | 1950               | ***     |

\* Stirrer stopped overnight.

\*\* Materials of three identical 4 mole runs combined.

\*\*\* In place of epichlorohydrin, 3468 g of crude fluorodinitroethyl glycidyl ether recovered from  $\text{CCl}_4$  extraction of crude 1,3-bis(fluorodinitroethoxy)isopropanol of runs 1, 2, and 3 was used. At an assumed purity of 75%, this amounts to 12.6 moles of the ether.

Table 3. 1,3-Bis(fluorodinitroethoxy)acetone (Pilot Runs)

| Run No. | FDNE, moles | Yield of crude alc., g | Yield of extracted alc., g | Yield of extract g | Wt of crude Ketone, g | Wt of chromat. Ketone, g | Wt of cryst. Ketone, g | Remarks |
|---------|-------------|------------------------|----------------------------|--------------------|-----------------------|--------------------------|------------------------|---------|
| 1       | 12          | 1611                   | 840                        | 770                | 626                   | 324                      | 193                    |         |
| 2       | 20          | 2854                   | 1584                       | 1246               | 1247                  | 586                      | 365                    |         |
| 3       | 20          | 2402                   | 1290                       | 1110               | 1008                  | 594                      | 369                    |         |
| 4       | 12          | 1100                   | not extr.                  | -                  | 880                   | 314                      | 190                    |         |
| 5       | 12          | 2871                   | 1950                       | 866                | 1654                  | 830                      | 540                    | *       |

Total 1657

Overall yield (based on FDNE) = 12.1%

\* Recovered crude fluorodinitroethyl glycidyl ether (ca 12 moles), rather than epichlorohydrin was used in this run to synthesize the isopropanol derivative.

used directly in an oxidation reaction below.

1,3-Bis(fluorodinitroethoxy)acetone

The individual batches of prepurified 1,3-bis(fluorodinitroethoxy)isopropanol above were oxidized with Jones reagent in the same manner as in the laboratory operation. The crude ketone was purified in 600-800 g batches in a 4"x 7' glass column containing 10-11 kg of activated silica gel using methylene chloride as eluent. No problems were encountered with the scale-up and the data is summarized in Table 3.

Column-purified 1,3-bis(fluorodinitroethoxy)acetone, contaminated mainly with 1-(fluorodinitroethoxy)-3-chloroacetone, was crystallized from chloroform to give a white crystalline solid, mp 37°. The over-all yield of crystalline 1,3-bis(fluorodinitroethoxy)acetone based on fluorodinitroethanol employed in the synthesis of 1,3-bis(fluorodinitroethoxy)isopropanol, amounted to ca 12% in these large-scale runs.

1,3-Bis(fluorodinitroethoxy)-2,2-bis(difluoramino)propane (SYEP)

Approximately five pounds of SYEP was produced in a scale-up production consisting of eight 0.5-0.75 lb runs. The results of these runs are summarized in Table 4. A remotely operated shielded reactor used in this scale-up work is described in The Experimental Section. Except for somewhat more elaborate instrumentation, this apparatus was essentially an enlarged version of the

Table 4. SYEP (Pilot Runs)

| Run No. | HNF <sub>2</sub> Generator charge |       |  | Reactor charge |                                    |             |       |                                      | SYEP  |         | Remarks |
|---------|-----------------------------------|-------|--|----------------|------------------------------------|-------------|-------|--------------------------------------|-------|---------|---------|
|         | Difluorourea Sol'n                |       | Conc H <sub>2</sub> SO <sub>4</sub> ml | 30% Oleum ml   | CH <sub>2</sub> Cl <sub>2</sub> ml | Ketone      |       | CH <sub>2</sub> Cl <sub>2</sub> , ml | g     | % yield |         |
|         | ml                                | moles |  |                |                                    | g           | mol   |                                      |       |         |         |
| 1       | 1500                              | 2.2   | 750                                    | 260            | 360                                | 181         | 0.5   | 725                                  | 224.3 | 100     |         |
| 2       | 1500                              | 2.2   | 275                                    | 260            | 360                                | 181         | 0.5   | 725                                  | 225   | 100     |         |
| 3       | 1700                              | 2.6   | 350                                    | 325            | 450                                | 227         | 0.627 | 950                                  | 278   | 97      |         |
| 4       | 1700                              | 2.6   | 350                                    | 325            | 450                                | 227         | 0.627 | 950                                  | 281   | 99      |         |
| 5       | 1700                              | 2.6   | 350                                    | 325            | 450                                | 227         | 0.627 | 950                                  | 276   | 98      |         |
| 6       | 1700                              | 2.6   | 350                                    | 325            | 450                                | 262         | 0.724 | 950                                  | 323   | 99      |         |
| 7       | 1700                              | 2.6   | 350                                    | 325            | 450                                | 262         | 0.724 | 950                                  | 282   | 86      | *       |
| 8       | 3400                              | 5.2   | 700                                    | 750            | 900                                | {227<br>226 | 1.251 | 1900                                 | 347   | 61.5    | **      |

\* The yield and purity of this batch of SYEP were adversely affected by insufficient amount of difluoramine in the reactor caused by a bad batch of difluorourea. The yield of purified product amounted to only 141 g (43%).

\*\* Stirring in the reactor was very poor in this run. Yield of purified material, 291 g (52%).

laboratory scale apparatus.

Generally, no problems were encountered in the synthesis of SYEP on this larger scale. SYEP of 98+<sup>4</sup>% purity in 97-100% yields was obtained in the first six 0.5-0.75 lb scale runs. In the next run, the yield and the purity of SYEP was poor, and the problem was traced to an insufficient amount of difluoramine in the reactor, caused by an incompletely fluorinated batch of urea. The results of the last run intended for a further scale-up to 1.7 lb of SYEP were also unsatisfactory because of the stirrer failure.

The two impure SYEP batches were purified by passing the material through an acidic alumina column using methylene chloride as the eluent. A sizable amount of SYEP was lost during the process of this purification.

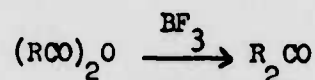
For all practical purposes, SYEP can be obtained quantitatively in the difluoramination of 1,3-bis(fluorodinitroethoxy)acetone. Since the yields of oxidation and difluoramination reactions are essentially quantitative, the very low yield in fluorodinitroethanol-epichlorohydrin reaction is solely responsible for the relatively low over-all yield of SYEP.

## SECTION IV

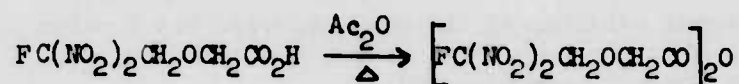
### MISCELLANEOUS REACTIONS

While the objective of this program was to synthesize SYEP by the process described in detail in preceding sections, a few other potential routes to the compound were briefly explored, and the results are summarized here.

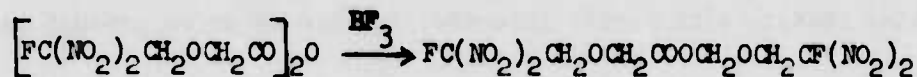
It is reported by Man and Houser (Ref. 11) that symmetrical ketones can be synthesized in good yields by self-condensing of anhydrides by a Friedel Crafts catalyst, usually boron trifluoride:



This route was investigated for the synthesis of 1,3-bis(fluorodinitroethoxy)-acetone. The starting material for this reaction, fluorodinitroethoxyacetic anhydride, was obtained in 60% yield by reacting fluorodinitroethoxyacetic acid (Ref. 8) with acetic anhydride:



The anhydride, a white crystalline solid, was characterized by elemental analysis and nmr spectra. Under the reaction conditions employed by Man and Houser, however, fluorodinitroethoxyacetic anhydride reacted with boron trifluoride to give fluorodinitroethoxymethyl fluorodinitroethoxyacetate, rather than 1,3-bis(fluorodinitroethoxy)acetone:

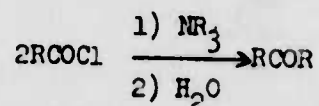




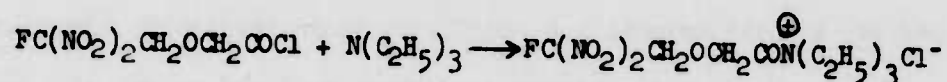
The compound was identified by elemental analysis and its nmr spectra.

A small amount of a side reaction product identified as fluorodinitroethoxymethyl acetate was also obtained in the above reaction. The acetate was most likely produced because of a small amount of acetic anhydride present as the contaminant in fluorodinitroethoxyacetic anhydride.

Another related potential route to 1,3-bis(fluorodinitroethoxy)acetone based on a work reported by Sauer (Ref. 12) was explored. In this work, Sauer reported excellent yields of symmetrical ketones by reacting two moles of an acid chloride with trialkylamines:



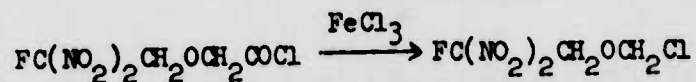
Since fluorodinitroethoxyacetyl chloride is readily available (Ref. 8), its reaction with triethylamine was briefly explored. This reaction, however, did not yield 1,3-bis(fluorodinitroethoxy)acetone either. A white crystalline solid obtained when an ethereal solution of the acid chloride was treated with the amine appeared to be the acyl ammonium salt:



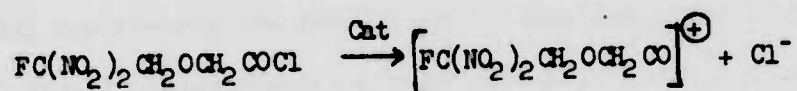
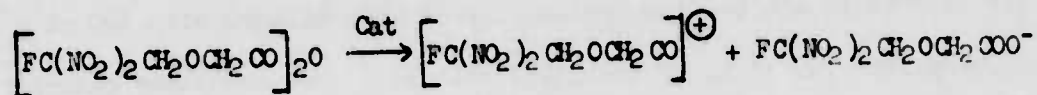
Attempts to synthesize 1,3-bis(fluorodinitroethoxy)acetone from fluorodinitroethoxyacetyl chloride using a Friedel Crafts catalyst, analogous to the reactions of acid anhydrides reported by Man and Houser, also failed. The acid chloride reacted readily with ferric chloride, but the reaction product was



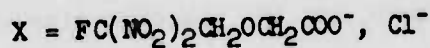
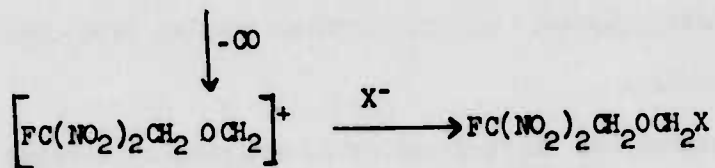
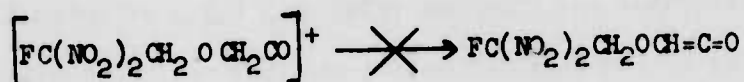
chloromethyl fluorodinitroethyl ether, rather than the desired ketone:



The reactions of fluorodinitroethoxyacetic anhydride and fluorodinitroethoxyacetyl chloride with Friedel Crafts catalysts seem to be related and apparently proceed through the common intermediate, fluorodinitroethoxyacylium ion:



The intermediate ion was expected to lose a proton and yield a ketone intermediate which, after dimerization and decarboxylation, should give 1,3-bis-fluorodinitroethoxy)acetone. Instead, these negatively substituted acylium intermediates underwent decarbonylation to the fluorodinitroethoxymethyl carbenium ion which reacted with fluorodinitroethoxyacetate or chloride anions:



## SECTION V

### EXPERIMENTAL

1,3-Bis(fluorodinitroethoxy)isopropanol (From Fluorodinitroethyl Glycidyl Ether). To a stirred and cooled solution of 9.3 g (0.06 mol) of fluorodinitroethanol and 20 ml of methanol in 110 ml of 37% aqueous formaldehyde was added dropwise at 15-20° a solution of 2.65 g (0.04 mol) of 85% potassium hydroxide in 5 ml of water and then 10.5 g (0.05 mol) of fluorodinitroethyl glycidyl ether. The mixture was stirred at ambient temperature for 66 hrs, diluted with 100 ml of water, and extracted with 30 ml of methylene chloride. The methylene chloride layer was washed with 100 ml of water and dried. The solvent was removed and the residual oil, 8.7 g, containing 1,3-bis(fluorodinitroethoxy)isopropanol, fluorodinitroethyl glycidyl ether, and oxymethylene polymer, was distilled at 100° (0.2 mm). The distillate amounting to 2.7 g was mainly the glycidyl ether, and the distillation residue, 5.6 g, contained the isopropanol derivative contaminated with oxymethylene polymers. Approximately 60% of the glycidyl ether was destroyed in this reaction.

When the above reaction was repeated using only 0.5 g of potassium hydroxide, very little of the isopropanol derivative was produced. The extract contained mainly the unreacted glycidyl ether. Similar results were obtained using 1.0 g of potassium hydroxide.

Yet another experiment was carried out using the same conditions as the first run above, but the reaction time was reduced from 66 hrs to 22 hrs. The

composition of the crude reaction mixture and yields were about the same as above.

1,3-Bis(fluorodinitroethoxy)isopropanol (From Epichlorohydrin) Laboratory Scale. To a stirred and cooled solution of 308 g (2.0 moles) of fluorodinitroethanol and 80 g (0.865 mol) of epichlorohydrin in 500 ml of 37% aqueous formaldehyde at 20-23° was added a cold solution of 82 g (2.05 moles) sodium hydroxide in 80 ml of water, and 0.6 g of methyl tricapryl ammonium chloride. The initially clear solution was stirred at ambient temperature for 68 hrs. The reaction mixture was diluted with 500 ml of water and extracted with 200 ml of methylene chloride. The extract was washed with 500 ml of 10% aqueous sodium hydroxide solution followed by two 500 ml portions of water. The dried solution was concentrated on a rotating evaporator to give 165 g of crude product. The proton nmr spectrum showed that the isopropanol derivative was contaminated with fluorodinitroethyl glycidyl ether, 1-(fluorodinitroethoxy)-3-chloroisopropanol, and a large amount of polyoxymethylene products. The crude material was distilled at 95-100° (0.3 mm) and volatile contaminants, including most of the glycidyl ether were removed. The distillation residue amounting to 140 g was distilled in a small falling film apparatus at 100° (0.1 mm) and another 35 g of distillate, mainly the glycidyl ether, was removed. The distillation residue, 105 g, contained the isopropanol derivative and polyoxymethylene.

Another identical experiment yielded 168 g of crude product which after distillation left 103 g of crude 1,3-bis(fluorodinitroethoxy)isopropanol.

1,3-Bis(fluorodinitroethoxy)isopropanol (KBr<sub>4</sub> Reduction). A stirred and cooled (dry ice-acetone) reactor was charged with a solution of 10 g (0.0276 mol) of crystallized 1,3-bis(fluorodinitroethoxy)acetone in 30 ml of methanol. Over a period of 2 hrs a solution of 0.745 g (0.015 mol) of potassium borohydride in 20 ml of cold water containing 0.1 ml of 10% aqueous sodium hydroxide, and a solution of 100 ml of 6 N sulfuric acid were added simultaneously at 20° in such a manner that the pH of the reaction mixture remained at 3-4 throughout the run. The mixture was stirred overnight at room temperature, diluted with 100 ml of water, and extracted with 35 ml of methylene chloride. The methylene chloride layer was dried and evaporated on a rotating evaporator to leave 8.65 g (85% yield) of bis(fluorodinitroethoxy)isopropanol identified by its nmr spectra ( Ref.3).

1,3-Bis(fluorodinitroethoxy)acetone (Laboratory Scale). The 105 g batch of crude degassed 1,3-bis(fluorodinitroethyl)isopropanol above was dissolved in 750 ml of acetone. Jones reagent prepared from 64 g of concentrated sulfuric acid, 40 g (0.4 mol) of chromium trioxide and 80 ml of water was added dropwise with stirring at 22-26° (4 hrs) to this solution. The reaction mixture was allowed to stand at ambient temperature overnight and was filtered. The filter cake was washed with three 100 ml portions of acetone. The filtrate and washings were combined and concentrated to ca 150 ml on a rotating evaporator. The concentrate was washed with 200 ml of water and was dissolved in 100 ml of methylene

chloride. The methylene chloride solution was washed with two 150 ml portions of water and was dried over anhydrous sodium sulfate. The solvent was removed to give 85 g of crude ketone contaminated (nmr) with polyoxymethylenes.

The crude isopropanol derivative of the 103 g run above was oxidized in an identical manner to give 91 g of crude ketone.

Purification of Crude 1,3-Bis(fluorodinitroethoxy)acetone (Laboratory Scale). Crude 1,3-bis(fluorodinitroethoxy)acetone prepared in the first batch above (85 g) was purified by column chromatography using a 2-1/4" OD column containing 1 kg of activated silica gel (Davison, Grade 12, 28-200 mesh), eluting with methylene chloride. Residues from 500 ml fractions were as follows.

| <u>Fraction No.</u> | <u>Weight of product, g</u> | <u>nmr spectrum</u>                        |
|---------------------|-----------------------------|--|
| 1                   | 1.0                         | yellow liquid; no ketone                   |
| 2                   | 0.5                         | - " -                                      |
| 3 }                 | 2                           | ketone and chloroketone                    |
| 4 }                 |                             |  |
| 5 }                 | 13                          | - " -                                      |
| 6 }                 |                             |  |
| 7 }                 |                             |  |
| 8 }                 | 19                          | good quality ketone +<br>some chloroketone |
| 9 }                 |                             |  |
| 10 }                |                             |  |
| 11 }                |                             |  |
| 12 }                | 12                          | good quality ketone;<br>less chloroketone  |
| 13 }                |                             |  |
| 14 }                |                             |  |
| 15 }                |                             |  |
| 16                  | 2.0                         | - " -                                      |
| 17 }                | 7.0                         | good quality ketone                        |
| 18 }                |                             |  |
| 19 }                |                             |  |
| 20                  | 0.5                         | - " -                                      |

The products of fractions 3-20 were combined to give 55 g of column-purified 1,3-bis(fluorodinitroethoxy)acetone contaminated with 1-(fluorodinitroethoxy)-3-chloroacetone. From nmr spectra it is estimated that the mixture contained 33 to 40 g of 1,3-bis(fluorodinitroethoxy)acetone which is ca 10% yield based on fluorodinitroethanol.

The other batch of crude 1,3-bis(fluorodinitroethoxy)acetone prepared above (91 g) was purified in an identical manner to give 57 g of column purified mixture of the two ketones of about the same composition as that above.

1,3-Bis(fluorodinitroethoxy)isopropanol (Pilot Scale). To a stirred and cooled (ice-water bath) solution of 3080 g (20 moles) of fluorodinitroethanol and 1000 g (10.8 moles) of epichlorohydrin in 6 l of 37% aqueous formaldehyde was added at 20-23° dropwise (45 min) a cold solution of 820 g (40.5 moles) of sodium hydroxide in 800 ml of water and 2.5 g of methyl tricapryl ammonium chloride. The mixture was stirred at 22-25° for 46 hrs, diluted with 4 l of water and extracted with 4 l of methylene chloride. The methylene chloride solution was washed with three 4 l portions of water and was dried over anhydrous sodium sulfate. The solvent was removed on a rotating evaporator to leave 2855 g of crude product. The proton nmr spectrum showed that the isopropanol was contaminated with large amounts of fluorodinitroethyl glycidyl ether, 1-(fluorodinitroethoxy)-3-chloroisopropanol, and polyoxymethylene.

The crude material was placed in a liquid-liquid extractor and extracted with carbon tetrachloride to a constant volume (12 hrs). The material freed



from carbon tetrachloride on a rotating evaporator weighed 1584 g. Its proton nmr spectrum showed that practically all the glycidyl ether was extracted. This still highly contaminated material was oxidized to 1,3-bis(fluorodinitroethoxy)acetone (see below).

The carbon tetrachloride extract above was concentrated (50° at 20 mm) to leave 1246 g of a pale liquid which (nmr) contained mainly fluorodinitroethyl glycidyl ether but also a considerable amount of polyoxymethylene polymers.

1,3-Bis(fluorodinitroethoxy)acetone (Pilot Scale). Crude 1,3-bis(fluorodinitroethoxy)isopropanol above, 1584 g, was dissolved in 9 liters of acetone. To the stirred and cooled (ice-water bath) solution was added dropwise at 10-12° over a period of 7 hrs 4.4 moles of the Jones reagent prepared by adding 383 ml of concentrated sulfuric acid to a solution of 440 g of chromium trioxide in 860 ml of water. After standing at 10-15° overnight, the mixture was filtered and the filter cake was washed with four 600 ml portions of acetone. The filtrate and washings were combined and bulk of acetone was removed on a rotating evaporator of 50-70° at 20 mm. The residue was diluted with 1.5 l of methylene chloride and washed with four 1.5 l portions of water. The methylene chloride solution was dried and solvent was removed to leave 1248 g of crude 1,3-bis-(fluorodinitroethoxy)acetone contaminated with polyoxymethylene.

The crude ketone was divided into two approximately equal portions and purified by column chromatography as follows.

A 4"x 5' glass column containing methylene chloride was packed with 10.5 kg

of desiccant grade silica gel (Davison, Grade 12, 28-200 mesh) and 623 g of the crude ketone was eluted with methylene chloride. Following fractions were collected.

| Fraction | Volume of eluent, ml | Total volume of eluent, l | Wt of product, g | nmr                 | Wt of cryst. ketone g |
|----------|----------------------|---------------------------|------------------|---------------------|-----------------------|
| 1        | 14                   | 14                        | 1.0              | impurities          |                       |
| 2        | 46                   | 60                        | 250              | good quality ketone |                       |
| 3        | 16                   | 76                        |                  | highly imp.         | 186                   |
| 4        | 20                   | 96                        | 40               |                     | did not crystallize   |
| 5        | 10                   | 106                       | 2                | impurities          |                       |

Chromatography of the second aliquot of the crude ketone gave similar results. The chromatographed material contained large amounts of 1-(fluorodinitroethoxy)-3-chloroacetone as the major impurity, which remained in solution when the product was crystallized from chloroform. 1,3-Bis(fluorodinitroethoxy)acetone is a white crystalline solid, mp 37°.

1,3-Bis(fluorodinitroethoxy)-2,2-bis(difluoramino)propane (SYEP) Laboratory Scale. The following apparatus was assembled in a fume hood and the operator was protected by heavy glass shields.

An aqueous solution of N,N-difluorourea, 250 ml (ca 0.35 mole of N,N-difluorourea) was placed in a magnetically stirred three-necked round-bottomed flask (generator) heated by a water bath and equipped with a dropping funnel containing 60 ml of concentrated sulfuric acid, a gas inlet tube, and a reflux condenser. The top of the condenser was connected to an ice-water cooled trap which in turn was attached to a Drierite drying tube. The drying tube was connected in series

to a magnetically stirred 100 ml four-necked round-bottomed flask (reactor) with a bottom opening stopcock cooled by an ice-water bath. The flask was fitted with a dry-ice acetone condenser, the exit of which was connected to a liquid bubbler, a hypodermic syringe connected by means of spaghetti Teflon tubing and a thermometer. In the reactor was placed 22 ml of 30% fuming sulfuric acid and 30 ml of methylene chloride. The whole system was flushed with nitrogen and a slow stream of the gas was maintained throughout the run. Difluoramine was generated by allowing the concentrated sulfuric acid to flow slowly (20 min) to the stirred difluorourea solution and heating at 85-90° for 15-20 minutes. Difluoramine was absorbed by oleum in the reactor. The oleum was stirred for additional 20 minutes and a solution of 1,3-bis(fluorodinitroethoxy)acetone (15 g, 0.041 mol) in 70 ml of methylene chloride was introduced slowly (20 min) from the syringe into the reactor. There was a mild exotherm and the reaction temperature increased to 10-15°. The cooling bath was lowered and the reaction was allowed to proceed at ambient temperature for 2 hrs. The stirring was stopped and the phases were allowed to separate. The organic phase (top layer) was drained (remotely) into 200 ml of water. The methylene chloride-water mixture was stirred overnight and the organic layer was then washed with four 150 ml portions of water. Solvent was boiled and replenished until the distillate did not oxidize KI paper. The methylene chloride solution was dried over anhydrous sodium sulfate and passed through a pad of silica gel. A small aliquot of the clear and colorless solution was evaporated on a rotating evaporator in order to determine the amount

of SYEP produced, 18.4 g (97.3% yield).

Proton nmr ( $\text{CDCl}_3$ ):  $\delta$  4.58 (d,  $J_{\text{HF}} = 16$  Hz, 4 H,  $2\text{FC}(\text{CH}_2)_2-$ ) and 4.16 (a broadened singlet, 4 H,  $-\text{CH}_2\text{C}(\text{CH}_2)-$ ) ppm; fluorine nmr:  $\phi$  110.1 (a poorly resolved triplet, 2F,  $2\text{FC}-$ ) and -27.9 (a broadened singlet, 4F,  $2\text{NF}_2$ ) ppm.

Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{N}_2\text{F}_6\text{O}$ : C, 18.67; H, 1.79; N, 18.67. Found: C, 18.44; H, 1.58; N, 17.91.

Pilot Scale. Apparatus for producing 0.5 to 1 lb of SYEP was installed behind 5/8" steel barricades containing a 2" thick safety glass view window and equipped with remote control arms. Basic features of this all glass apparatus were essentially the same as that of the laboratory set except for its size and the following somewhat more elaborate controls. A vacuum pump was attached to the system for a faster evacuation. Five liter three-necked flasks were used as the difluoramine generator and as the reactor. The reflux condenser above the generator was cooled by circulating ice-water and that above the reactor by a circulating acetone at  $-60^\circ$ . All temperatures were measured by thermocouples. Because of poor visibility through the view window an interface sensor was installed in the drain stopcock of the reactor for easy separation of phases at the end of a run. This sensor, containing platinum electrodes and connected to a power supply and detection circuits, measured the conductivity of the solution flowing through the stopcock. A sharp sudden decrease in conductivity signalled the phase interface.

This apparatus, operated in the same manner as the small laboratory scale

unit, was employed without any safety incidents to synthesize 5 lbs of SYEP in 8 separate runs amounting to 0.5 to 0.75 lb of the material per run.

Allyl Fluorodinitroethyl Ether. To a stirred and cooled (ice-water bath) solution of 50 ml of methanol and 31 g (0.2 mol) of fluorodinitroethanol in 50 ml of 37% aqueous formaldehyde was added at 16-18° a solution of 9 g (0.225 mole) of sodium hydroxide in 10 ml of water. To the resulting solution was added 28 g (0.23 mol) of allyl bromide and the mixture was stirred at 20-22° for 5.5 hrs. The mixture was diluted with 100 ml of water and extracted with 75 ml of methylene chloride. The methylene chloride solution was washed with 100 ml of cold 5% sodium hydroxide followed by two 100 ml portions of water. Methylene chloride was removed from the dried solution to give 24.5 g (63% yield) of crude allyl fluorodinitroethyl ether. The crude material was distilled to give 21.5 g of pure allyl fluorodinitroethyl ether (55.4% yield).

Oxidation of Allyl Fluorodinitroethyl Ether with MCPA. Crude allyl fluorodinitroethyl ether as obtained above, 117 g (0.6 mol), was dissolved in 300 ml of chloroform and the solution was placed in magnetically stirred one liter three-necked round-bottomed flask equipped with an efficient reflux condenser and a thermometer. To the solution was added 122 g of 85% m-chloroperbenzoic acid (MCPA) (0.6 mol) and the resulting solution was warmed in a water bath to 50°. A mildly exothermic reaction began at this temperature and the heating bath was removed. The reaction temperature gradually increased to

63-65° but could be controlled by a reflux condenser. m-Chlorobenzoic acid gradually deposited. After 1 hr when the exothermic reaction subsided the mixture was refluxed for 30 min and then cooled to 5-10°. The mixture was filtered and the filter cake was washed with three 40 ml portions of cold (5-10°) chloroform. The material was air dried to give 88 g of m-chlorobenzoic acid.

The filtrate and washings above were combined and washed with 400 ml of saturated aqueous sodium bicarbonate solution and with 300 ml of water. The chloroform solution was dried and stripped of solvent to give 115 g (91% yield) of fluorodinitroethyl glycidyl ether.

Fluorodinitroethoxyacetic Anhydride. A solution of 10 g (0.0472 mol) of fluorodinitroethoxyacetic acid (Ref. 8) in 15 ml of acetic anhydride was refluxed for 8 hrs and the excess of acetic anhydride and acetic acid were removed under reduced pressure. The reaction product, 8.3 g, was contaminated with fluorodinitroethoxyacetic acid which was removed by distillation at 175-180° (0.1 mm). The degassed material amounting to 6.1 g (64% yield) solidified at room temperature and was crystallized from carbon tetrachloride to give 5.1 g of a white crystalline solid, mp 54°.

Proton nmr ( $\text{CDCl}_3$ ):  $\delta$  4.32 (d,  $J_{\text{HF}} = 16 \text{ Hz}$ ; 4 H,  $2\text{FCH}_2^-$ ) and 4.69 (s, 4 H,  $2-\text{CH}_2\text{COO}-$ ) ppm.

Anal. Calcd for  $\text{C}_8\text{H}_8\text{F}_2\text{N}_4\text{O}_{13}$ : C, 23.66; H, 1.98. Found: C, 23.42; H, 2.03.

Fluorodinitroethoxymethyl Fluorodinitroethoxyacetate. A slow stream of



boron trifluoride was passed at 0° for ca 50 min into a stirred and cooled solution of 4 g (0.01 m) of fluorodinitroethoxyacetic anhydride in 3 ml of chloroform. The resulting mixture was added to a solution of 4 g of sodium acetate in 9 ml of water and heated at 95-100° for 45 min. Chloroform was allowed to evaporate. The cooled mixture was extracted with 25 ml of methylene chloride and the methylene chloride solution was washed with 50 ml of saturated aqueous sodium bicarbonate solution followed by 50 ml of water. The methylene chloride solution was dried and stripped to give 2.2 g of oil. The crude material was distilled at 150° (0.1 mm) in a short-path micro distillation apparatus to give 1.9 g of fluorodinitroethoxymethyl fluorodinitroethoxyacetate, a colorless oil.

Proton nmr ( $\text{CDCl}_3$ ):  $\delta$  5.25 (s, 2 H,  $-\text{COOCH}_2\text{O}-$ ), 4.62 and 4.68 (two doublets,  $J_{\text{HF}} \approx 16$  Hz, 4 H,  $2\text{F}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{CH}_2-$ ), and 4.23 (s, 2 H,  $-\text{OCH}_2\text{COO}-$ ) ppm.

Anal. Calcd for  $\text{C}_{12}\text{H}_8\text{F}_2\text{N}_4\text{O}_{12}$ : C, 22.24; H, 2.13. Found: C, 22.36; H, 2.18.

A few drops of a colorless liquid obtained as a forerun in the above distillation was identified as fluorodinitroethoxymethyl acetate.

Proton nmr ( $\text{CDCl}_3$ ):  $\delta$  5.17 (s, 2 H,  $-\text{COOCH}_2-$ ), 4.66 (d,  $J_{\text{HF}} = 16$  Hz, 2 H,  $\text{F}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{CH}_2-$ ), and 2.10 (s, 3 H,  $\text{CH}_3$ ) ppm.

Anal. Calcd for  $\text{C}_7\text{H}_7\text{F}_2\text{N}_2\text{O}_7$ : C, 26.56; H, 3.12. Found: C, 27.3; H, 3.14.

#### Reaction of Fluorodinitroethoxyacetyl Chloride with Aluminum Chloride.

Gas was evolved immediately when 0.3 g of anhydrous aluminum chloride was added to 1.0 g (0.047 mol) of fluorodinitroethoxyacetyl chloride. When evolution of

gas ceased in ca 10 min, the mixture was washed with 10 cc of ice water and extracted with 10 ml of methylene chloride. The extract was distilled to give 0.85 g of a colorless liquid, bp 40° (0.2 mm), identified as chloromethyl fluorodinitroethyl ether by comparing its physical properties and its proton nmr spectrum with those of an authentic sample of the ether (Ref. 13).

Reaction of Fluorodinitroethoxyacetyl Chloride with Triethylamine. To a stirred and cooled (0-5°) solution of 2.3 g (0.01 mol) of fluorodinitroethoxyacetyl chloride (Ref. 8) in 70 ml of diethyl ether was added dropwise (15 min) a solution of 1.0 g (0.01 mol) of triethylamine in 15 ml of diethyl ether. A white crystalline solid precipitated instantaneously. The mixture, protected from moisture by a calcium chloride drying tube, was refluxed for 24 hrs, cooled, and filtered. The filter cake, washed with ether, amounted to ca 3 g. The filtrate and washings were combined and evaporated to dryness on a rotary evaporator. There was no residue in the evaporation flask.

## SECTION VI

### CONCLUSIONS AND RECOMMENDATIONS

1,3-Bis(fluorodinitroethoxy)-2,2-bis(difluoramino)propane, SYEP, a new energetic plasticizer, was synthesized by difluoramination of 1,3-bis(fluorodinitroethoxy)acetone, and the compound was fully characterized. Preliminary results at Fluorochem, RPL, and Lawrence Livermore Laboratory indicate that SYEP possesses suitable chemical and physical properties for a high energy plasticizer.

The bottleneck step in the production of SYEP is the synthesis of 1,3-bis(fluorodinitroethoxy)isopropanol in the reaction between fluorodinitroethanol and epichlorohydrin. A brief study of reaction parameters failed to improve significantly the low 12-15% yield.

The synthesis of the isopropanol derivative from fluorodinitroethanol and fluorodinitroethyl glycidyl ether is unattractive because an additional step is needed. Furthermore, the glycidyl ether is obtained in only 30-35% yields and its reaction with fluorodinitroethanol is equally poor. Synthesis of fluorodinitroethyl glycidyl ether in 55-60% yields by oxidation of allyl glycidyl ether with m-chloroperbenzoic acid explored in this work requires yet another additional step and was eliminated as too costly.

Considering all presently available alternatives, the one step synthesis of 1,3-bis(fluorodinitroethoxy)isopropanol is still the most economical and was employed in this work.

Production of 1,3-bis(fluorodinitroethoxy)isopropanol requires large amounts of expensive fluorodinitroethanol and affects unfavorably the economics of the whole process. Since a considerable amount of work has already been reported on the reactions of fluorodinitroethanol with epoxides, it seems unlikely that the yield in this step could be significantly improved simply by manipulating such variables as reagent ratios, reaction temperature and reaction time. Rather it is apparent that a basic study based on novel approaches is needed. It is, for example, conceivable that catalysts could be found or developed which would significantly improve the yields of fluorodinitroethanol reactions with epoxides. Such catalysts are well known in the reactions of epoxides with normal alcohols.

The purification of crude 1,3-bis(fluorodinitroethoxy)acetone by column chromatography, a relatively expensive operation, is another lesser problem of the present SYEP process. It is possible that if the yield of 1,3-bis(fluorodinitroethoxy)isopropanol could be improved as discussed above, a better quality ketone would result in the oxidation step, and the crude material maybe could be purified by crystallization. In the present work a few batches of crude ketone could be crystallized without column purification.

One safety problem in the present SYEP process is the use of highly flammable acetone as the solvent in the oxidation of 1,3-bis(fluorodinitroethoxy)isopropanol. For relatively small scale work, this high-yield simple procedure is acceptable, but these oxidation conditions would present a drawback in a large scale production of SYEP. Other oxidizing agents and condi-

tions have not been explored extensively during this work, and a nonflammable solvent would be preferable for large scale work.

## SECTION VII

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## SECTION VIII

### LIST OF ABBREVIATIONS

|      |   |
|------|---|
| FDNE | 2-Fluoro-2,2-dinitroethanol                               |
| FEFO | Bis(fluorodinitroethyl)formal                             |
| MCPA | <u>m</u> -Chloroperbenzoic Acid                           |
| RPL  | Rocket Propulsion Laboratory, Edwards Air Force Base      |
| SYEP | 1,3-Bis(fluorodinitroethoxy)-2,2-bis(difluoramino)propane |

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